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International Journal of Inorganic Materials 3 (2001) 1185–1187

International Journal of Inorganic Materials

Importance of soft solution processing for advanced $BaZrO_3$ materials

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Abstract

Barium zirconate is an interesting material for refractory applications as well as a good substrate for the manufacturing of high temperature superconductors. However, its solid state synthesis requires high temperature and provides inhomogeneous powder with a broad particle size distribution. In order to avoid these disadvantages, soft solution routes are of growing importance in the ceramic powder synthesis. Precipitation, decomposition of precursors, combustion techniques offer alternative ways to the solid state method. Advantages of these are a lower calcination temperature, production of homogeneous and fine monodisperse powders. The obtained powders have been characterised by XRD, IR, SEM and DTA/TG analysis. The influence of the synthesis conditions on the properties of $BaZrO_3$ has been studied. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Barium zirconate; Soft solution processing; Characterization

1. Introduction

Ceramic materials are used for a wide variety of applications where high purity powders with well-controlled composition and properties are of highest importance. To overcome the drawbacks of conventional solid state syntheses, solution processing has gained much interest and has proved to give better results. Different solution processes have been tested for the preparation of $BaZrO_3$. Barium zirconate is an interesting material for the refractory industry as well as a good substrate for the manufacturing of high temperature superconductors due to its structural compatibility and chemical inertia towards the melts [1]. In order to produce dense substrates, a high purity powder with a well controlled size distribution is necessary.

We investigated the preparation of $BaZrO_3$ powders by (1) the chemical decomposition of an oxalate precursor, (2) the chemical decomposition of a citrate precursor, (3) the precipitation in the presence of urea and finally by (4) a combustion technique using oxalic dihydrazide as the fuel [2]. The products were characterised by X-ray diffraction analysis, IR Fourier Transform spectroscopy, thermal analysis, optical and electronic microscopies, and compared to the powders obtained by the classical solid state route. The scope of this study is to make a general evaluation of different soft solution syntheses.

2. Experimental procedure

Five different methods have been used in order to produce a suitable precursor powder of the expected $BaZrO_3$ phase.

2.1. Oxalate method

Basic zirconium carbonate hydrate (3 g, 1 M) was dissolved in dilute nitric acid (1.5 M, 10 ml). This solution was added to a solution of ammonium oxalate in molar excess of 10% (2.2 M) with respect to barium and zirconium. A 1 M solution of $Ba(NO_3)_2$ was then added under continuous stirring. The resulting precipitate was separated from the solution by centrifugation. Tests for the presence of barium ions in the supernatant solution were negative.

2.2. Citrate method

Basic zirconium carbonate hydrate was dissolved under gentle heating in a 1.5 M solution of nitric acid. The cooled solution (0.4 M) was added to a solution of citric acid (0.8 M). A gel like white precipitate was formed but was redissolved upon addition of concentrated ammonia. The pH was brought to 7 with concentrated ammonia. A solution of barium nitrate (0.4 M) was added slowly under constant stirring to the previous solution. Addition of an excess of methanol leads to the quantitative precipitation of the mixed complex.

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PII: S1466-6049(01)00122-2

2.3. Precipitation in the presence of urea

A solution of $BaCl_2$ was added to a solution of $ZrOCl_2$ in order to obtain a mixed solution. The total concentration of cations in the mixed solution was kept at 0.5 M. Then 50 ml of this mixed solution was added to 25 ml of distilled water containing 15 g of urea. The solution was heated to 90°C at which the urea decomposition occurs and maintained at this temperature for 60 h under stirring. A white precipitate was isolated by centrifugation and washed twice with de-ionised water and finally dried at 100°C for 12 h before the calcination step.

2.4. Combustion using oxalic dihydrazide

Stoichiometric amounts of barium and zirconium carbonates were dissolved separately in 1.5 M nitric acid under gentle heating. These solutions were mixed together to obtain a solution 0.5 M in each cation. Twenty wt% oxalic dihydrazide [$NH_2NH(CO)_2NHNH_2$] with respect to the total mass of barium and zirconium salts was added to the solution and a gentle heating was performed until dissolution of the solid. The solution was maintained 3 h in an oven at 200°C to initiate the ignition.

2.5. Solid state synthesis

Stoichiometric amounts of barium carbonate and zirconium oxide were mixed together in an agate mortar with petroleum ether.

The different precursor powders were simultaneously heat-treated in a muffle furnace. The decomposition of the dried precipitate was studied by TG-DSC (NETZCH 449C) with a heating rate of 10°C/min. The phase analysis was performed using X-ray diffraction. IR spectra were taken on the precursor powders and calcined products. Particle size and morphology of the powder were examined using scanning electron microscopy.

3. Results and discussion

From the thermal analyses of the different powders we deduce that the temperature required for the formation of a pure $BaZrO_3$ phase depends on the nature of the precursor. The lowest temperature is obtained for $BaZrO_3$ prepared by the combustion synthesis. Results obtained for oxalate and citrate decomposition are quite similar. A calcination at 1000°C is necessary. A calcination temperature of 1200°C is necessary both for the powders prepared in the presence of urea and for the conventional mixed oxides solid state reaction. Yet the holding time for the former is shorter (1 h versus 5 h).

In the case of oxalate and citrate methods, X-ray diffractograms of the 900°C material correspond to pure $BaZrO_3$ phase (Fig. 1a). Although TGA measurement shows a weight loss occurring between 900 and 1000°C or 1100°C (for the oxalato complex, Fig. 1b), this has been attributed to the presence of adsorbed or entrapped CO_2 (see below).

The decomposition of $BaZrO(C_2O_4)\cdot xH_2O$ and $BaZrO(C_6H_6O_7)_2\cdot xH_2O$ follows the same procedure. The reaction proceeds in three-steps [3,4] i.e. dehydration, decomposition of the complex to form carbonate species and decomposition of the carbonates. The decomposition process involves the appearance of $BaCO_3$ that further reacts with an amorphous ZrO_2. Indeed no crystallised ZrO_2 can be detected in the different diffractograms. The intermediate formation of $BaCO_3$ is confirmed by IR spectrum (Fig. 2) and X-ray diffraction analysis. In the case of precipitation in the presence of urea, $BaCO_3$ is the only crystalline phase present in the precipitate. Zirconium precipitates as a zirconium hydroxide amorphous gel in which the particles of $BaCO_3$ are embedded.

Fourier transform infrared spectra taken on the different products reveals the presence of carbonates in the calcined powders. The degree of carbonation depends on the calcination temperature being the slightest for the powder

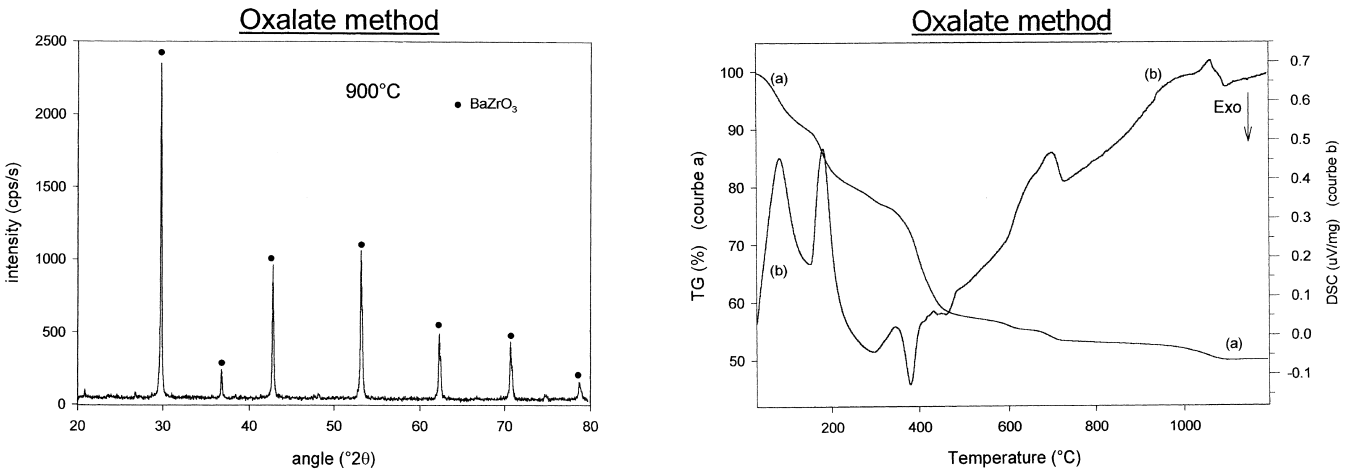

Fig. 1. XRD pattern (left) and TGA/DSC curve (right) in the case of the oxalate method.

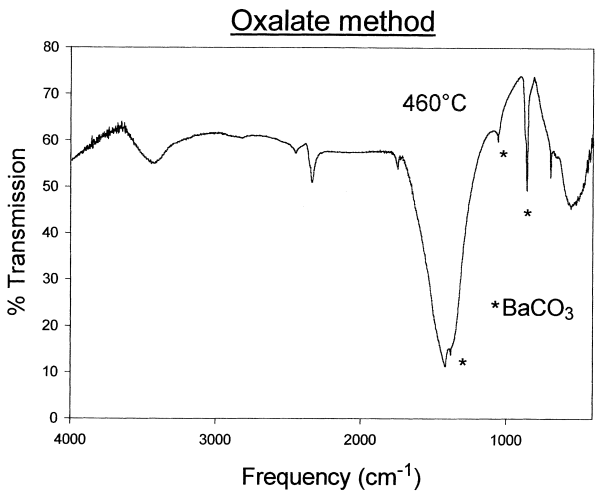

Fig. 2. FTIR spectrum of the oxalato complex heat treated at 460°C/3 h.

calcined at 1200°C. But it also depends on the preparation mode. The $BaZrO_3$ prepared by combustion using oxalic dihydrazide was less carbonated than the powders obtained by the decomposition of oxalate and citrate complexes. Carbonate bands are due to the adsorption of CO_2 forming $BaCO_3$ at the surface of the powders. The presence of carbonates might induce porosity upon sintering due to the evolution of CO_2 gases. It also leads to a powder whose composition is not known exactly and whose behaviour in slip casting and upon sintering might change from batch to batch.

In the case of precipitation in the presence of urea and solid state synthesis, the endothermic transitions observed around 800 and 950°C are attributed to crystallographic transitions for $BaCO_3$: $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ that theoretically take place at 810°C and 970°C respectively [5]. The successive appearance of the different phases of $BaCO_3$ are also observed on the X-ray diffraction patterns.

The powders prepared by the different synthesis were observed using scanning electron microscopy. The particles are round shaped in all cases (Fig. 3). Yet, the agglomerates are larger in the case of the solid state synthesis. The powders prepared by soft solution processes present a more homodispersed size distribution. The smallest particles are obtained by precipitation in the presence of urea and by combustion, with particles having an average size of 0.2 μ.

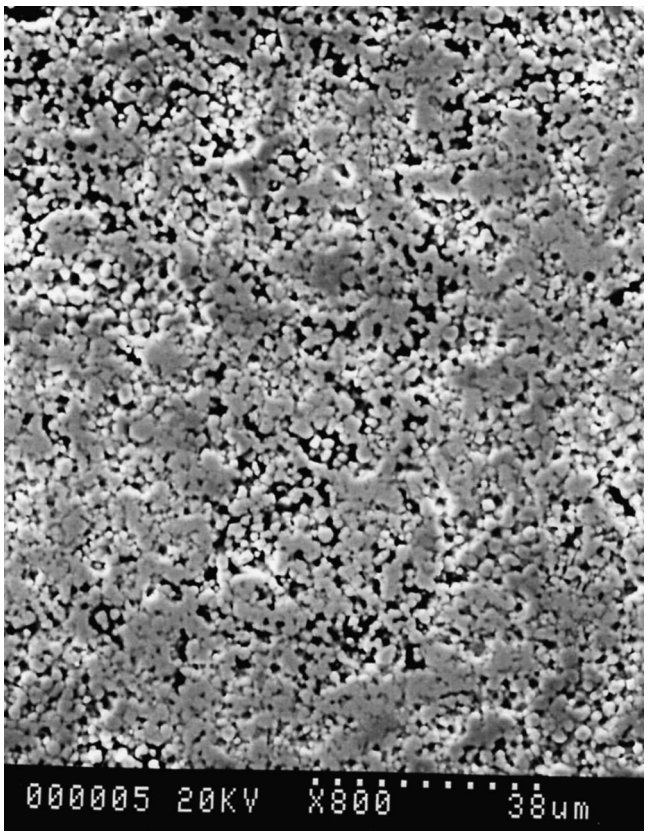

Fig. 3. Electron micrograph of BaZrO3 synthesised by the oxalate method at 900°C/6 h.

4. Conclusions

The soft solution processes are promising methods for preparation of ceramic powders. The main advantages are: A lower calcination temperature, homogeneous powders, monodispersed small size particles and spherical particles. The combustion with oxalic dihydrazide is particularly of interest as it leads to the lower calcination temperature and to less carbonated $BaZrO_3$ phase. Optimisation of the different parameters involved in this method is currently under investigation. The $BaZrO_3$ powders obtained by the different syntheses reported here have to be compared regarding their sintering ability. The green bodies are expected to have a better density than green bodies obtained for powders prepared by solid state synthesis as fine powders are advisable for the manufacturing of dense ceramic substrates.

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